Methanation on K^+-modified Pt/SiO_2: the impact of reaction conditions on the effective role of the promotor

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This paper reports on the first study that the authors know of of the effect of alkali promotion of Pt on methanation. Methanation was investigated on a 4.5 wt% Pt/SiO_2 catalyst promoted with different amounts of K^+ ($K^+/Pt = 0, 0.1$, and 0.2) for two different temperature ranges (503–552 K and 573–665 K). The methanation rate was 10–70% lower on the promoted catalysts for reaction temperatures of 573 to 665 K. In this temperature range, the relative decrease in rate upon promotion was a function of K^+ loading and did not vary with temperature, p_{H_2}, p_{CO}, or time-on-stream. In addition, there was no significant effect of K^+-promotion on activation energy (ca. 29 kcal/mol) or methanation reaction orders with respect to CO and H_2 (−0.1–0.0 and 0.4–0.6, respectively). However, there was a decrease in the number of methane-destined surface intermediates upon promotion as determined by steady-state isotopic transient kinetic analysis (SSITKA). All these observations lead to the conclusion that, in this higher reaction temperature range, K^+ acts mainly as a site-blocking agent for methanation on Pt and does not change the reaction rate of the limiting step, probably hydrogenation. Between 503 and 552 K, the activation energy and reaction orders with respect to H_2 and CO were also not affected by K^+. However, the catalyst with a K^+/Pt ratio of 0.1 showed the highest methanation activity. In this lower temperature range and for all the catalysts, the apparent activation energies were also found to be lower, 18 vs. 29 kcal/mol, compared to those at higher temperatures. The reaction order with respect to CO was higher (0.2–0.3) in comparison with what was observed in the higher temperature range (ca. −0.1–0.0). These results suggest, that, in the low temperature range and for low loadings of K^+, K^+ affects the rate-determining step resulting in a rate increase greater than the decrease due to the blockage effect. Thus, K^+ serves as a rate promoter at low reaction temperatures while its only effective function is site blockage at higher temperatures.

Keywords: methanation, Pt/SiO_2, potassium promotion, isotopic transient kinetic analysis, SSITKA

1. Introduction

In numerous studies, it has been found that alkali promotion can improve activity and/or selectivity of transition metal catalysts for CO hydrogenation [1,2]. Alkali additives are often used to promote chain-growth in Fischer–Tropsch synthesis [3]. Although much research has been undertaken in the past in order to better understand alkali promotion, the underlying mechanisms of this phenomenon are still not completely understood since promoting effects vary greatly with the catalyst, the alkali promoter, and the reaction products (CH_4 vs. MeOH, for example).

The methanation activity of Pt has been found to be orders of magnitude lower than that of Ru, Co, or Ni catalysts [4]. One main step in the mechanism of CO hydrogenation to form methane is the dissociation of CO on the catalyst surface. It is thought that the poor activity of Pt is related to the fact that CO does not dissociate readily on this metal [5]. While for Co, Ru and Ni, the rate-determining step (RDS) is usually found to be the hydrogenation of surface carbonaceous species, it has been suggested [6] that, for Pt, the rate-limiting step is C–O bond rupture, such as is the case for Fe. It has already been demonstrated that CO dissociation on group VIII metals can be facilitated by alkali additives [7]. This would suggest that an alkali-promoted Pt catalyst might be more active for CO hydrogenation than an unpromoted one. Unfortunately, no studies have been found in the literature concerning the alkali promotion of Pt for CO hydrogenation, perhaps due to the low inherent activity of Pt. However, such a system offers an interesting opportunity to test hypotheses about how alkali promoters affect CO hydrogenation on different metal surfaces.

Although there is a lack of results in the literature concerning the effect of potassium promotion of Pt on CO hydrogenation, the adsorption behaviors of H_2 and CO on potassium-covered Pt(111) have been studied extensively [8–11]. The sticking coefficient of CO has been found to decrease with increasing potassium loading due to a site-blockage effect of the potassium. The presence of the alkali on the Pt surface also induces a decrease in the strength of the carbon-to-oxygen bond and an increase in the CO adsorption energy, apparently in part due to short-range K–CO interactions. It has been observed that the heat of adsorption of CO may increase as much as 10–15 kcal/mol on most transition metals,

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including Pt, doped with alkali metals. The sticking coefficient for H_2 has been found also to decrease with increasing potassium surface coverage. In addition, the dissociation of H_2 on Pt has been reported to be enhanced and the heat of adsorption to increase with increasing potassium loading [11,12]. In summary, the changes observed in the adsorption behavior of CO and H_2 on alkali-doped catalysts have been attributed in large part to strong attractive interactions between the adsorbate and the promoter, possibly such as direct coupling and / or electrostatic interactions [12,13].

The objective of this study was to investigate the effects of K^+-promotion on methanation over Pt/SiO_2. The impact of K^+ was investigated at various temperatures and H_2 and CO partial pressures. In addition, the time-on-stream behaviors of the catalysts were studied using steady-state isotopic transient kinetic analysis (SSITKA). SSITKA is one of the most powerful kinetic techniques for studying reactions on high surface area heterogeneous catalysts. It permits in situ measurement of the concentrations and lifetimes of surface intermediates while maintaining steady-state reaction [14–16].

2. Methods

2.1. Catalyst preparation

The base Pt/SiO_2 catalyst was prepared from hexachloroplatinic acid ($H_2PtCl_6{\cdot}5H_2O$, Aldrich, purity 99.995%), dissolved in distilled water, using the incipient wetness method and SiO_2 (Davison, grade 952, surface area 219 m^2/g). One cm^3 of solution per gram of SiO_2 was added, resulting in a 4.5 wt% Pt/SiO_2 catalyst after drying and reduction. The catalyst was dried overnight at 390 K. Reduction of the catalyst was carried out in flowing hydrogen (purity 99.999%). The temperature was kept constant at 393 K for 30 min, at 533 K for 30 min, and at 723 K for 1 h, with temperature ramping of 1°C / min between plateaus. The catalyst was cooled down to room temperature in hydrogen, purged with helium (purity 99.999%) for 30 min, and passivated during 4 h with 50 cm^3 / min of 1.5% oxygen in helium.

The potassium-promoted catalysts were prepared from this reduced and passivated base catalyst in order to maintain constant Pt dispersion using the incipient wetness method and a potassium nitrate (EM Science company, grade PX1520-1) aqueous solution. Distilled water was used for impregnation of the unpromoted catalyst. Two promoted catalysts were prepared, having K^+/Pt atomic ratios of 0.1 and 0.2. They were reduced and passivated in the same way as the base catalyst. Since the potassium is present in cationic form, it is identified by K^+ in this paper rather than K. In order to simplify the notation, the promoted catalysts are referred to in this paper as KPt.1 and KPt.2, whereas the base catalyst is denoted by KPt.0.

2.2. Catalyst characterization

Elemental analysis was done by Galbraith Laboratories, Inc. A Pt loading of 4.5% for all the catalysts was determined by atomic absorption. The K^+/Pt ratios of KPt.1 and KPt.2 were found to be 0.1 and 0.2, respectively. Using CO chemisorption at room temperature and an assumption of $CO/Pt_s = 1$, the Pt dispersion on KPt.0 was determined to be 24%. This corresponds to an average Pt particle size of 2.5 nm.

2.3. Reaction system

A schematic representation of the reaction system can be found in ref. [17]. The catalyst was placed in a quartz micro-reactor with i.d. of 4 mm. A thermocouple was installed at the top of the catalyst bed. For the SSITKA measurements a pneumatic valve operated electronically was used to switch between feed streams containing different isotopic labeling of the reactant species (^{12}CO vs. ^{13}CO). The pressure was maintained constant for the two streams being switched by using two back pressure regulators. The on-line analytical part of the system consisted of a gas chromatograph (Varian 3700 GC) and a mass spectrometer (Leybold-Inficon Auditor 2 MS). In the GC the products were separated by a 6-foot, 60–80 mesh Porapak Q column and detected with a flame ionization detector (FID). The mass spectrometer was equipped with a high-speed data-acquisition system interfaced to a personal computer. The hold-up of the gases in the entire system was minimized. The lines of the outlet streams were heated to 150°C in order to avoid the possibility of heavy product deposition and blockage. All the gases used for this study were of ultra high purity grade from Praxair, except ^{13}CO which was obtained from Isotec. Before entering the reaction system, H_2 and CO were further purified using an Alltech Gas Purifier packed with indicating Drierite and 5A molecular sieve and a Matheson 450 Purifier filled with 4A molecular sieve, respectively.

2.4. Kinetic measurements

Rate measurements of methanation were made using 25 to 35 mg of catalyst loaded into the flow microreactor. The catalyst was rereduced in situ with the same procedure employed for the initial reduction described above. After rereduction, the catalyst bed temperature was lowered to the desired reaction temperature and the feed was switched to the reaction mixture. Methanation was carried out from 503 to 552 K and from 573 to 665 K at 2.6 bar total pressure (1 bar = 10^5 Pa). The total flow rate was kept at 22 cm^3 / min for all the experiments. The partial pressures of H_2 and CO normally used for temperature dependency study were 1.2 and 0.1 bar, respectively, with the balance being He. However, for the study of the effects of partial pressure, the partial pressure of H_2 was varied between 0.6 and 2.4 bar, holding the partial pressure of CO at 0.2 bar, and the partial pressure of CO was varied between 0.2 and 1.4 bar, holding the partial pressure of H_2 at 1.2 bar.

Reaction data were collected after 5 min of reaction in order to study the catalyst surface in its most pristine state. At these conditions the conversion was kept very low (less than 1.3% in all cases) and differential reactor behavior could be assumed. At this space velocity and the reaction conditions utilized, mass and heat transport limitations were not detected. Specific activities were determined and are reported in terms of rate of CH_4 formation per gram of catalyst as opposed to TOF, due to the effects that the promoter can have on CO chemisorption measurements. After each reaction period, the catalyst was bracketed with H_2 in order to ensure consistently a clean catalyst surface for kinetic characterization at the different reaction temperatures. After each set of experiments, the activity was remeasured at the first reaction conditions to check for any irreversible deactivation of the catalyst. For the temperature dependence study, the kinetic measurements were taken with decreasing temperature. Time-on-stream behavior was studied at 665 K and partial pressures of H_2 and CO of 2.4 and 0.2 bar, respectively.

In the time-on-stream studies, steady-state isotopic transients were taken by switching between two feed streams where the only difference was the isotopic composition of CO: one stream containing ^{12}CO and the other ^{13}CO. A trace of argon (5%) was present in the ^{12}CO stream in order to measure the gas-phase holdup of the entire reaction system. This was not enough to disrupt the reaction during the isotopic switches. Isotopic transients could not be measured in the low temperature range where the extremely low concentration of product was below the sensitivity limit of the mass spectrometer.

3. Results

3.1. Activity and selectivity

The CH_4 selectivity during CO hydrogenation on all the catalysts studied, as determined by gas chromatography, was 100%. In tables 1–4, one can see that the reaction rates on all the platinum catalysts were very low, even at high temperatures. This is consistent with the work of Vannice [4], who found that Pt has a low activity for methanation. Figure 1 shows a typical Arrhenius plot for the unpromoted catalyst. The apparent activation energies for all the catalysts in the two temperature ranges are displayed in table 5. It is worthwhile to note the lower apparent activation energies measured in the low temperature range (503–588 K) compared to that in the higher temperature range (645–665 K), ca. 18 vs. 29 kcal/mol, respectively. This does not seem to be due to an exothermic effect, since an acceptable linearity in the Arrhenius plot is observed for both temperature ranges.

Table 1
Influence of the CO partial pressure on the rate of methanation at 523 K ($P_{H_2} = 1.2$ bar)

Catalyst	P_{CO} (bar)	R_M [a] (10^{-3} μmol/(g-cat. s))
KPt.0	0.2	1.5
	0.5	1.9
	0.7	2.0
	1.4	2.8
KPt.1	0.2	2.0
	0.5	2.4
	0.7	2.7
	1.4	3.1
KPt.2	0.2	1.4
	0.5	1.5
	0.7	1.6
	1.4	2.5

[a] Rate of methane formation: $\pm 0.1 \times 10^{-3}$ μmol/(g-cat. s)).

3.2. Effects of partial pressure of CO

At 523 K the reaction rate was consistently highest for KPt.1 and lowest for KPt.2 as CO partial pressure was varied (table 1). The reaction order in CO was ca. 0.3 for all the catalysts (table 5). At 665 K the rates of reaction on the promoted catalysts were all lower than those of the unpromoted catalyst (table 2). The reaction order in CO at this temperature was ca. −0.1 (table 5).

3.3. Effects of partial pressure of H_2

At 523 K the reaction rate was also consistently highest for KPt.1 and lowest for KPt.2 as H_2 partial pressure was varied (table 3). The reaction order in H_2 was ca. 0.5

Table 2
Influence of the CO partial pressure on the rate of methanation at 665 K ($P_{H_2} = 1.2$ bar)

Catalyst	P_{CO} (bar)	R_M [a] (10^{-3} μmol/(g-cat. s))
KPt.0	0.2	490
	0.5	520
	0.7	520
KPt.1	0.2	300
	0.5	290
	0.7	260
	1.4	220
KPt.2	0.2	160
	0.5	150
	0.7	140
	1.4	130

[a] Rate of methane formation, $\pm 3 \times 10^{-3}$ μmol/(g-cat. s).

Table 3
Influence of the H_2 partial pressure on the rate of methanation at 523 K ($P_{CO} = 0.2$ bar)

Catalyst	P_{H_2} (bar)	R_M [a] ($10^{-3}\mu$mol/(g-cat. s))
KPt.0	0.6	1.2
	1.0	1.6
	1.4	2.0
	2.4	2.4
KPt.1	0.6	1.6
	1.0	1.7
	1.4	2.3
	2.4	3.0
KPt.2	0.6	0.9
	1.0	1.0
	1.4	1.1
	2.4	1.4

[a] Rate of methane formation, $\pm 0.1 \times 10^{-3}$ μmol/(g-cat. s).

for all the catalysts (table 5). At 665 K the rates of reaction on the promoted catalysts were all lower than those of the unpromoted catalyst at all partial pressures of H_2 (table 4). The reaction order in H_2 was also ca. 0.5 for all the catalysts at this higher temperature (table 5).

3.4. *Effects of time-on-stream*

Figure 2 displays the methanation rate at 665 K as a function of time-on-stream (TOS) for KPt.1 and the unpromoted catalyst. The rate of KPt.1 was about 20% lower than that of the unpromoted catalyst (table 6). The activities of both catalysts decreased relatively sharply during the initial 60 min of TOS, the relative decrease in activity being comparable. In terms of SSITKA parameters (table 6), τ_{CO}, the average surface residence time of adsorbing–desorbing CO was constant within experimental error with TOS for both catalysts (0.5 and 0.4 s for KPt.0 and KPt.1, respectively). N_{CO}, the surface concentration of CO, was also constant within experimental error with TOS for both catalysts (20 and 16 μmol/g-cat. for KPt.0 and KPt.1, respectively). τ_M, the average surface residence time of all carbon-containing intermediates leading to methane, remained constant or at most decreased slightly within experimental error for both catalysts. τ_M for KPt.1 appears to have been slightly lower than that for KPt.0. N_M for KPt.1 was systematically lower compared to the unpromoted catalyst. For both catalysts, N_M decreased significantly with TOS during the first 60 min. As mentioned earlier, the SSITKA measurements could not be made in the lower temperature range due to the low activities of all the catalysts.

Table 4
Influence of the H_2 partial pressure on the rate of methanation at 665 K ($P_{CO} = 0.2$ bar)

Catalyst	P_{H_2} (bar)	R_M [a] ($10^{-3}\mu$mol/(g-cat. s))
KPt.0	0.6	370
	1.0	420
	1.4	530
KPt.1	0.6	320
	1.0	370
	1.4	490
KPt.2	0.6	110
	1.0	120
	1.4	150
	2.4	180

[a] Rate of methane formation: $\pm 3 \times 10^{-3}$ μmol/(g-cat. s).

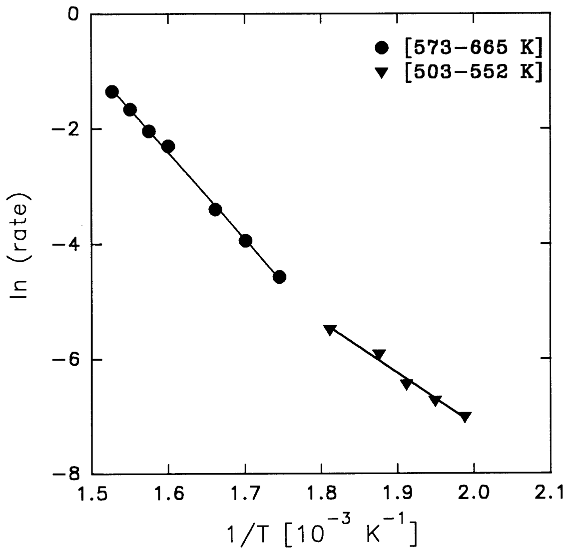

Figure 1. Arrhenius plot for KPt.0 ($P_{H_2} = 2.4$ bar, $P_{CO} = 0.2$ bar).

4. Discussion

It has been previously shown that modifiers have numerous ways of affecting catalyst and reaction behaviors. The major proposed mechanisms of how modifier adspecies affect catalytic systems are (a) electronic interactions with the catalytic site, (b) direct interaction with reactants, (c) electrostatic field effects, (d) site blockage, and (e) surface reconstruction. It is, however, often difficult to assign one single mechanism of action for a modifier since in many cases modifiers may affect a catalyst in several ways simultaneously. Furthermore, the mechanism of promotion may also be strongly dependent on the reaction conditions.

4.1. *High temperature range (573–665 K)*

K^+-promotion caused a uniform decrease in the methanation rate in this temperature range (tables 2 and 4). It can be seen in tables 2 and 4 that the ratios of the

Table 5
Apparent activation energies and power law exponents for the two temperature ranges (P_{CO} = 0.2 bar, P_{H_2} = 2.4 bar)

Catalyst	E^{app} (kcal/mol) [a]		Exponent of P_{H_2}		Exponent of P_{CO}	
	503–552 K	573–665 K	523 K	665 K	523 K	665 K
KPt.0	20	27	0.5	0.4	0.3	0.0
KPt.1	20	29	0.5	0.6	0.2	−0.1
KPt.2	17	29	0.6	0.4	0.3	−0.1

[a] Apparent activation energy: ±2 kcal/mol.

activities of the promoted catalyst to the unpromoted catalyst remained more or less constant throughout all measurements as partial reactant pressure was varied. As shown by the TOS study (figure 2), the relative deactivation during TOS in the reaction rate was comparable for both KPt.0 and KPt.1. The stronger adsorption of CO on K^+-promoted Pt and increased dissociation [1,8,10] apparently does not lead to either an increase in reaction rate or rate of deactivation. It would appear that K^+ does not have a long-range effect on carbon transformation on the metal sites not blocked by K^+, otherwise there should have been a change in the rate of deactivation upon K^+-promotion. Instead, the K^+-free metal sites appeared to deactivate with no effects from K^+. This phenomenon is similar to the one observed in K^+-modified Ru catalysts [18].

In order to understand the reason for the significant decrease in rate upon K^+-promotion in this temperature range, it is useful to analyze the results obtained from the isotopic transients during time-on-stream sampling. As seen in table 6, the inverse of the average surface residence time of the carbon-containing methane intermediates, $1/\tau_M$, which is a good estimate of "true" TOF, was slightly higher for KPt.1. This may indicate, that the average intrinsic activity of a Pt active site was somewhat greater upon promotion under these conditions. However, the surface concentration of methane intermediates (N_M) decreased significantly with K^+-addition (table 6). This suggests that, the dominant role of K^+ as a Pt modifier for methanation in the higher temperature range is to block active sites.

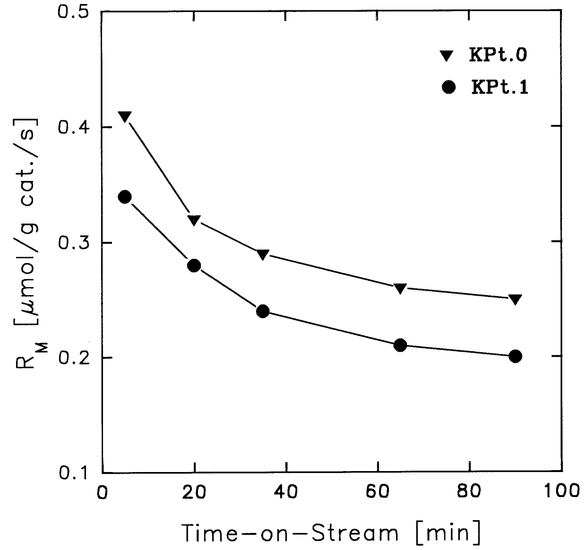

Figure 2. Dependence of reaction rate on time-on-stream (P_{H_2} = 2.4 bar, P_{CO} = 0.2 bar, T = 665 K).

4.2. Low temperature range (503–552 K)

The major difference in the methanation results for this temperature range is that KPt.1 showed a higher activity overall than the unpromoted catalyst (KPt.0) (tables 1 and 3). The blockage effect is apparently more than compensated by another promotion mechanism. By looking closer at the kinetic parameters, one can observe that the main differences between the two temperature ranges were a somewhat lower apparent activation energy in the lower temperature range (table 5) and a higher reaction order with respect to CO (0.3 vs. −0.1–0.0) at higher temperatures. The reaction order with respect to H_2 was similar for both temperature ranges (0.5). Literature values for apparent activation energies of methanation vary between 15 and 25 kcal/mol for group VIII metals [19]. Metals like Ru or Co, where the rate-determining step is hydrogenation of surface carbon, tend to have apparent activation energies ranging towards the upper limit; whereas metals like Pt, Pd or Fe have generally lower apparent activation energies. It may be suggested that the lower activation energy in the low temperature range (18 vs. 29 kcal/mol) is symptomatic of a difference in the reaction mechanism, perhaps due to an increased importance of CO dissociation relative to the other elementary steps.

A widely accepted mechanism proposed by a number of different authors, such as those of refs. [20,21], can be described simplistically by the following sequence of elementary steps:

$$CO + * \rightleftharpoons CO* \qquad (I)$$

$$CO* + * \rightleftharpoons C* + O* \qquad (II)$$

$$H_2 + 2* \rightleftharpoons 2H* \qquad (III)$$

$$C* + H* \rightarrow CH* + * \qquad (IV)$$

Table 6
Effects of time-on-stream on SSITKA parameters ($P_{H_2} = 2.4$ bar, $P_{CO} = 0.2$ bar, $T = 665$ K)

	TOS (min)	R_M [a] (10^{-3} μmol/(g-cat. s))	τ_{CO} [b] (s)	N_{CO} [c] (μmol/g-cat.)	τ_M [b] (s)	$1/\tau_M$ (s^{-1})	N_M [d] (μmol/g-cat.)
KPt.0	5	410	0.5	20	1.20	0.8	0.50
	20	320	0.5	20	1.00	1.0	0.32
	35	290	0.5	20	0.80	1.3	0.23
	65	260	0.5	20	1.10	0.9	0.28
	90	250	0.5	20	0.90	1.1	0.22
KPt.1	5	340	0.4	16	1.10	0.9	0.38
	20	280	0.4	16	0.90	1.1	0.25
	35	240	0.4	16	0.70	1.4	0.17
	60	210	0.4	16	0.60	1.7	0.13
	90	200	0.4	16	0.70	1.4	0.14

[a] Rate of methane formation: $\pm 3 \times 10^{-3}$ μmol/(g-cat. s).

[b] Average surface residence time: ± 0.1 s.

[c] Surface concentration of CO: $\pm 10\%$.

[d] Surface concentration of carbon-containing intermediates leading to methane: $\pm 10\%$.

$$CH* + H* \rightarrow CH_2* + * \qquad (V)$$

$$CH_2* + H* \rightarrow CH_3* + * \qquad (VI)$$

$$CH_3* + H* \rightarrow CH_4 + 2* \qquad (VII)$$

$$2H* + O* \rightleftharpoons H_2O + 3* \qquad (VIII)$$

The rate expressions derived in this study are not able to be easily accommodated by a Langmuir–Hinshelwood model based on the above elementary steps. If one of the hydrogenation steps of surface carbon (steps (IV) to (VII)) were to be the rate-determining step (RDS), the reaction order of CO and H_2 would be -1 and 0.5, respectively. On the other hand, if the CO dissociation step (step II) were to be the RDS, the reaction order with respect to CO would still be negative due to the CO adsorption term, while the reaction order with respect to H_2 would be $\leqslant 0$. Even if CO adsorption were to be assumed to occur dissociatively, the reaction order for H_2 would still be $\leqslant 0$.

Another hypothetical mechanism involves the modification of steps (II) and (IV) assuming the hydrogenation of CO on the surface into an enol form of type CHOH [6,22,23], the RDS being then dissociation of CHOH in the presence of surface hydrogen to form CH_x species:

$$CO* + 2H \rightleftharpoons CHOH* \qquad (IIA)$$

$$CHOH* + xH* \rightarrow CH_x* + x* + H_2O \qquad (IVA)$$

The rate expressions derived in this study could also not be accommodated by this approach without attributing non-integer values to x, which is very difficult to conceive physically.

This difficulty in reconciling the rate data in this study with a Langmuir–Hinshelwood rate expression may be due to an oversimplification of the process by the assumptions inherent in Langmuir–Hinshelwood derivations: (a) one single rate-determining step with the other steps being in pseudo-equilibrium and (b) site homogeneity. It may be that in this case, several elementary steps are simultaneously rate-determining. From the reaction orders with respect to CO and H_2 derived in this study, it can be suggested that H_2 and CO are both involved in one of the rate-determining steps. However, it is not possible from the power law rate expression obtained from the data to establish whether methane formation on Pt under the conditions studied proceeds strictly by hydrogenation of molecular carbon monoxide or by hydrogenation of surface carbon coming from CO dissociation. On the other hand, it is well established [24,25] that CO dissociation on group VIII metals is facilitated by potassium. Since in the low temperature range the highest methanation activity is observed for KPt.1, it can be postulated that, under these conditions, the dominant role of the alkali may be to promote the methanation process by increasing the rate of CO dissociation. This promotion of CO dissociation in the presence of K^+ can be explained by a decrease in the carbon–oxygen bond strength for adsorbed CO already observed in numerous studies [8,9] and suggested by theoretical work [13]. It is also highly possible that this CO dissociation is hydrogen assisted based on the reaction order of H_2. For KPt.2, however, the site blockage effect outweighs any promotion of CO dissociation resulting in a loss in activity relative to lower K^+ loadings. As already, mentioned above, in the high temperature range, for both promoted catalysts, the major impact of K^+ appears to be the blocking of active methanation sites.

5. Conclusions

The influence of K^+-modification of Pt/SiO_2 catalysts on methanation was studied at two different temperature ranges, supported by SSITKA measurements.

– Between 573 and 665 K, the methanation activity decreased upon K^+-promotion. This effect did not vary significantly with temperature, time-on-stream, or partial pressures of CO and H_2. Based on the fact that the number of methane-destined surface intermediates showed a significant decrease upon promotion, it can be concluded that a simple site blockage mechanism is the predominant effect of K^+-promotion in this temperature range. At these reaction conditions K^+ did not appear to have any major impact on the rate-limiting step.

– Between 503 and 552 K, KPt.1 showed overall a higher methanation activity than the unpromoted catalyst. This was the case for all temperatures and partial pressures of H_2 and CO employed. It was further observed that the apparent activation energy was around 17–20 kcal/mol compared to 29–30 kcal/mol observed in the higher temperature range (573–665 K). The reaction order with respect to CO was 0.3 compared to ca. −0.1–0.0 observed at the higher temperature range. It was deduced that, for lower loading of K^+, in this low temperature range, K^+ affected the methanation mechanism resulting in a rate increase greater than the blockage effect. Based on our kinetic data, it is postulated that the major role of K^+ at the lower temperature range is to promote the methanation process by increasing the rate of a step involving CO dissociation which may involve hydrogen assistance.

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